

FORM PTO-1390 (Modified)
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

AD6530

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/486744INTERNATIONAL APPLICATION NO.
PCT/US98/18731INTERNATIONAL FILING DATE
8 September 1998 (08.09.98)PRIORITY DATE CLAIMED
8 September 1997 (08.09.97)

TITLE OF INVENTION

PACKAGING MATERIAL

APPLICANT(S) FOR DO/EO/US

TROUILHET, Yves

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☒ A change of power of attorney and/or address letter.
18. ☒ Certificate of Mailing by Express Mail
19. ☐ Other items or information:

17. General Power of Attorney**18. Express Mail Certificate EJ164303038US**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <div style="font-size: 2em; font-weight: bold; text-align: center;">09/486744</div>		INTERNATIONAL APPLICATION NO. <div style="text-align: center;">PCT/US98/18731</div>		ATTORNEY'S DOCKET NUMBER <div style="text-align: center;">AD6530</div>	
<div>20. The following fees are submitted:</div> <div>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</div> <div><div><input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO</div><div style="text-align: right;">\$840.00</div><div><input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482)</div><div style="text-align: right;">\$670.00</div><div><input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))</div><div style="text-align: right;">\$760.00</div><div><input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO</div><div style="text-align: right;">\$970.00</div><div><input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)</div><div style="text-align: right;">\$96.00</div></div> <div style="text-align: center; margin-top: 10px;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>				<div>CALCULATIONS PTO USE ONLY</div> <div style="border: 1px solid black; height: 150px; margin-top: 5px;"></div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <div style="display: inline-block; width: 100px;"></div> <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<div style="border: 1px solid black; padding: 2px;">\$840.00</div> <div style="border: 1px solid black; padding: 2px;">\$0.00</div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	7 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS				=	\$840.00
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).				<input type="checkbox"/>	\$0.00
SUBTOTAL				=	\$840.00
Processing fee of \$130.00 for furnishing the English translation later than <div style="display: inline-block; width: 100px;"></div> <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				+	\$0.00
TOTAL NATIONAL FEE				=	\$840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input checked="" type="checkbox"/>	\$40.00
TOTAL FEES ENCLOSED				=	\$880.00
				Amount to be:	
				refunded	\$
				charged	\$
<div><input type="checkbox"/> A check in the amount of _____ to cover the above fees is enclosed.</div> <div><input checked="" type="checkbox"/> Please charge my Deposit Account No. 04-1928 in the amount of \$880.00 to cover the above fees. A duplicate copy of this sheet is enclosed.</div> <div><input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 04-1928 A duplicate copy of this sheet is enclosed.</div>					
<div>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</div> <div>SEND ALL CORRESPONDENCE TO:</div> <div style="border: 1px solid black; padding: 5px; margin-top: 5px;"><div>EVANS, Craig H. E.I. DU PONT DE NEMOURS AND COMPANY LEGAL PATENT RECORDS CENTER 1007 MARKET STREET WILMINGTON, DELAWARE 19898 US</div></div> <div style="margin-top: 20px; text-align: right;"><div> SIGNATURE</div><div>EVANS, Craig H. NAME</div><div>31,825 REGISTRATION NUMBER</div><div>01 March 2000 DATE</div></div>					

TITLE

PACKAGING MATERIAL

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The present invention relates to packaging for food products that are sensitive to oxidation, including dairy products such as cheese, butter and margarine.

Background of the invention

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Various materials for providing oxygen barriers for products sensitive to oxidation are known, including ethylene vinyl alcohol (EVOH), amorphous nylon, semicrystalline polyamide 6 and polyacrylonitrile.

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For packaging liquid or semi-liquid materials that are sensitive to oxidation, water barrier properties are also needed. C.f. EP 0241 819, which discloses a laminate using nylon as a barrier; EP 0293 098, which discloses a multilayer structure with EVOH and low density polyethylene (LDPE) coated on board. More recently, EP 0520 767 discloses the use of amorphous nylon as a non-foil composite laminate. In all of these cases, water vapor transmission is below 10 g/m²d due to a relatively thick polyethylene seal layer.

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In soft cheese packaging the right balance of an oxygen barrier and a moisture barrier is given by a cellulosic film laminate to paper. In this case, the water vapor transmission is between 400 and 630 g/m²d at 38 °C and 90% relative humidity (RH), while the oxygen permeability is below 10 cc/m²d atm.

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Summary of the invention

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The present invention provides a flexible or semi-flexible packaging material with an oxygen barrier between 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at 38°C and 90% relative humidity comprising (a) a layer of paper having a weight between 20 and 400 g/m², (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m² adjacent to layer (a), and (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m² adjacent to layer (b). This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine.

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The packaging material may be made by means known in the art such as by coextrusion coating or lamination of coextruded film onto paper.

Detailed description of the invention

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As used herein, the following terms have the meanings given below.

'Flexible packaging material' means packaging sheet material suitable for wrapping goods, e.g. the aforementioned dairy products. 'Semi-flexible packaging material'

means packaging material having a somewhat higher resistance to flex, typically having a board (e.g. cardboard) as paper layer (a). Semi-flexible packaging material may be thermoformed, as known in the art, to form desired shapes, such as trays.

- 5 'Oxygen barrier' measures the rate at which oxygen passes through the packaging material of the present invention, and is between 10 and 100 cc/m²d atm measured according to ASTM D 3985.

- 10 'Water vapor barrier' measures the rate at which water vapor passes through the packaging material of the present invention, and is between 100 and 1000 g/m²d at 38°C and 90% relative humidity.

- 15 Paper layer (a) can be any type of paper typically used in the packaging industry, flexible or semi-flexible, and having a weight between 20 and 400 g/m². This weight governs the degree of flexibility of the paper. Paper, being a very porous material, does not control the oxygen or water vapor barrier properties of the packaging material of the present invention.

- 20 The ethylene copolymer of layer (b) can be ethylene vinyl acetate, ethylene-ethyl acrylate, ethylene-methyl acrylate or ethylene butyl acrylate, an ethylene-acid copolymer or its corresponding ionomer.

- 25 The ethylene-acid copolymers are copolymers of ethylene and α,β -ethylenically-unsaturated C₃-C₈ carboxylic acid have the acid moiety present in an amount of 1 to about 25, (preferably 6 to 9) wt. % of the copolymer. The preferred acid moieties are methacrylic acid and acrylic acid.

- 30 The ethylene-acid copolymers can also be E/X/Y copolymers where E is ethylene; X is a softening comonomer and Y is the α,β -ethylenically-unsaturated C₃-C₈ carboxylic acid, particularly acrylic or methacrylic acid. By "softening", it is meant that the polymer is made less crystalline. Suitable "softening comonomers (X) are monomers selected from alkyl acrylate, and alkyl methacrylate, wherein the alkyl groups have from 1 - 12 carbon atoms which, when present, may be up to 25 (preferably up to 15, most preferably up to 10) wt. % of the ethylene-acid copolymer.

- 35 Specific ethylene-acid copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate.

- 45 Corresponding ionomers of the ethylene-acid copolymers are formed by partially neutralizing the acid moiety. The acid moiety is partially neutralized with monovalent and/or bivalent metal cations such as lithium, sodium*, potassium, magnesium, calcium, barium, lead, tin, zinc* or aluminum (*= preferred), or a combination of such

cations. The mole percent of acid neutralized is up to about 70 %, preferably 30 to 50 %.

5 Ionomers can be made by processes well known in the art (cf. U.S. Pat. No. 3,262,272 to Rees, for example).

10 The graft of the ethylene copolymer will be maleic anhydride, typically in an amount between 0.1 and 3 weight %. Grafting can be carried out using techniques known in the art.

15 Optionally, layer (b) may further comprise up to 40 weight % of a copolyether ester, a copolyether amide or a polyurethane thermoplastic. Suitable copolyether esters are available under the name Hytrel® from the DuPont Company; suitable copolyether amides are available under the name Pebax® from Elf Atochem.

20 Layer (b) will be applied to paper layer (a) at a weight between 1 and 5 g/m² to assure the desired oxygen and water vapor barrier levels of the present invention are met. Suitable ethylene copolymers for use in layer (b) are the Bynel® and Surlyn® families of resins, both available from the DuPont Company.

25 Nylon layer (c) can contain pure amorphous nylon or can be a blend of between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6.

30 The term "amorphous polyamide" is well known to those skilled in the art. "Amorphous polyamide", as used herein, refers to those polyamides which are lacking in crystallinity as shown by the lack of an endotherm crystalline melting peak in a Differential Scanning Calorimeter ("DSC") measurement (ASTM D-3417), 10 °C/minute.

35 Examples of the amorphous polyamides that can be used include those amorphous polymers prepared from the following diamines: Hexamethylenediamine, 2-methylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, bis-(4-aminocyclohexyl)methane, 2,2-bis(4-aminocyclohexyl)isopropylidene, 1,4-diaminocyclohexane, 1,3-diaminocyclohexane, meta-xylylenediamine, 1,5-diaminopentane, 1,4-diaminobutane, 1,3-diaminopropane, 2-ethyldiaminobutane, 1,4-diaminomethylcyclohexane, p-xylylenediamine, m-phenylenediamine, p-phenylenediamine, and alkyl substituted m-pehnylenediamine and p-phenylenediamine.

40 Examples of polyamides that can be used include those amorphous polymers prepared from the following diacarboxylic acids: isophthalic acid, terephthalic acid, alkyl substituted iso- and terephthalic acid, adipic acid, sebacic acid, butane dicarboxylic acid, and the like.

45 Specific examples of amorphous polyamides which are suitable for this invention include: hexamethylenediamine isophthalamide, hexamethylenediamine isophthalamide/terephthalamide, copolymers of hexamethylene diamine and 2-

methylopentamethylenediamine with iso- or terephthalic acids, or mixtures of these acids. Polyamides based on hexamethylenediamine iso/terephthalamide containing high levels of terephthalic acid moiety may also be useful provided a second diamine such as 2-methyldiaminopentane is incorporated to produce a processible amorphous polymer.

The above amorphous polyamides may contain as comonomers minor amounts of lactam species such as caprolactam or lauryl lactam, even though polymers based on these monomers alone are not amorphous. The important feature is that the polyamide as a whole must be amorphous. Thus small amounts of these comonomers may be incorporated as long as they do not impart crystallinity to the polyamide. In addition, up to about 10 weight % of a liquid or solid plasticizer such as glycerol, sorbitol, mannitol, or aromatic sulfonamide compounds (such as Santicizer 8® from Monsanto) may be included with the amorphous polyamide.

A suitable amorphous polyamide for use in the present invention is available from the DuPont Company under the tradename SELAR®PA.

The term "semicrystalline polyamide 6" is well known to those skilled in the art. Semicrystalline polyamide 6 suitable for this invention are generally prepared from lactams or amino acids or from condensation of diamines such as hexamethylene diamine with dibasic acids such as sebacic acid. Copolymers and terpolymers of these polyamides are also included. A suitable semicrystalline polyamide 6 for use in the present invention is Durethan® B29, available from Bayer.

Layer (c) will be applied to paper layer (b) at a weight between 10 and 30 g/m² to assure the desired oxygen and water vapor barrier levels of the present invention are met.

This packaging material is particularly useful for packaging dairy products, such as cheese, butter and margarine. It will be typically be produced by coextrusion coating of layers (b) and (c) onto layer (a), or by lamination of extruded or coextruded layers (b) and (c) onto layer (a). Optionally, the so prepared packaging material can be subsequently thermoformed into a desired shape, such as a tray.

Example 1

Layer (b) of Bynel® 21E533 (an anhydride modified ethylene acrylate resin from DuPont) is coextruded with layer (c) of various blend of Selar® PA 3426 (an amorphous nylon from DuPont) and Durethan® B29 (a semicrystalline polyamide 6 from Bayer) and coated on paper.

The nylon blend is introduced into a 3.5" extruder with barrel temperatures set at 240, 280, 280, 280 and 280 °C. The Bynel® 21E533 is introduced in 2.5" extruder with barrel temperatures set at 180, 220, 250, 270, 280 °C. Feed bloc and die temperatures are set at 280°C.

The 800 mm wide die is 150 mm (air gap) above the nip where it coats the paper. The paper is corona treated and run at the line speed of 200 m/min. The final so produced structure is:

5	paper	//	The Bynel® 21E533	//	Selar® PA3426+Durethan® B29
	40 g/m ²		2 g/m ²		12 g/m ²

The following water transmission (38°C, 90% RH) and oxygen permeability (room temperature) is measured (% given by weight):

10	Example				water g/ m ² d	oxygen cc/ m ² d atm
	1.1	80% Selar® PA3426 + 20% Durethan® B29			400	32
15	1.2	50% “ + 50% “			500	35
	1.3	20% “ + 80% “			800	43

The last two structures are particularly well suited for soft cheese packaging.

20 Example 2

Example 1 is repeated except that Surlyn® AD2 is substituted for Bynel® 21E533.

25 Surlyn® AD2 (2 g/m²) is coextruded with the blend 80 weight % Selar® PA3426 + 20 weight % Durethan® B29 (12 g/m²). The oxygen permeability is the same as in Example 1.1. Water permeability lowers to 250 g/m²d.

This structure when extruded on a glossy chill-roll has a very glossy appearance. Together with the dead-foil, it can be used for candy and butter wrapping.

30 Example 3

35 Example 2 is repeated except that the paper layer is replaced with board having a weight of 200 g/m². The board can be thermoformed to produce trays or lidding.

Example 4

40 Example 1 is repeated except that the 70 wt. % Bynel® 21E533 and 30 wt % Hytrel® 3548 is substituted for Bynel® 21E533.

Claims

- 5 1. A flexible or semi-flexible packaging material with an oxygen barrier between 10 and 100 cc/m²d atm and a water vapor barrier between 100 and 1000 g/m²d at 38°C and 90% relative humidity comprising
- (a) a layer of paper having a weight between 20 and 400 g/m²
- 10 (b) a layer of ethylene copolymer or grafted ethylene copolymer having a weight between 1 and 5 g/m² adjacent to layer (a), and
- (c) a layer of nylon comprising between 5 and 100 weight % of amorphous nylon and 0 and 95 weight % semicrystalline polyamide 6 having a weight between 10 and 30 g/m² adjacent to layer (b).
- 15 2. The packaging material of claim 1 wherein the ethylene copolymer of layer (b) is ethylene vinyl acetate, ethylene-ethyl acrylate, ethylene-methyl acrylate or ethylene butyl acrylate.
- 20 3. The packaging material of claim 1 wherein the ethylene copolymer of layer (b) is an ethylene-acid copolymer or its corresponding ionomer.
4. The packaging material of claim 1 wherein the grafted ethylene copolymer of layer (b) is a maleic anhydride grafted ethylene copolymer.
- 25 5. The packaging material of any one of claims 1 to 4 wherein layer (b) further comprises up to 40 weight % of a copolyether ester, a copolyether amide or a polyurethane thermoplastic.
- 30 6. The packaging material of any one of claims 1 to 5 which is produced by coextrusion coating layers (b) and (c) onto layer (a).
- 35 7. The packaging material of any one of claims 1 to 5 which is produced by lamination of extruded or coextruded layers (b) and (c) onto layer (a).

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PACKAGING MATERIALS

the specification of which is attached hereto unless the following box is checked:

☒ was filed on **8 SEPTEMBER 1998** as U.S. Application No. _____ or PCT International Application No. _____
PCT/US98/18731 and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patent ability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Application No.	Country	Filing Date	Priority Claimed (Yes/No)
97 20 2750.2	EP	8 SEP 1997	Yes

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below.

U.S. Provisional Application No.	U.S. Filing Date

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patent ability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application No.	Filing Date	Status (patented, pending or abandoned)

POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Name: EVANS, CRAIG H.	Registration No. / 31,825
------------------------------	----------------------------------

Send correspondence and direct telephone calls to:

EVANS, CRAIG H.

E. I. du Pont de Nemours and Company
Legal - Patents
Wilmington, DE 19898, U.S.A.

Tel. No.
(302) 774-4919

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

INVENTOR(S)

Full Name of Inventor	Last Name TROUILLET	First Name YVES	Middle Name
	Signature (please sign full name): <i>Yves Trouillet</i>		Date:
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